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(54) **Optical wave-guides**

(57) Thermoplastically processable mixtures of from 0 to 95% by weight of polyamide-12, from 50 to 5% by weight of polyamide elastomers and from 0 to 95% by weight of other polyamides and/or copolyamides are used for the production of polymeric protective layers for optical wave-guides.

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Fig.A.

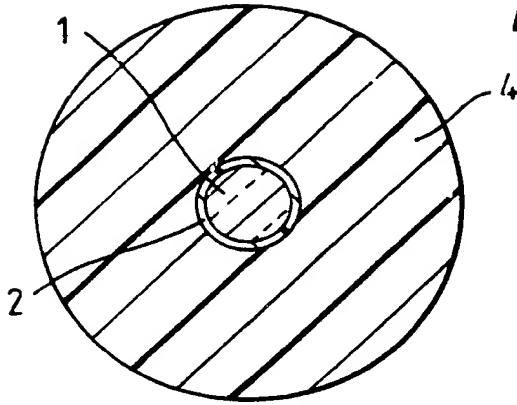


Fig.B.

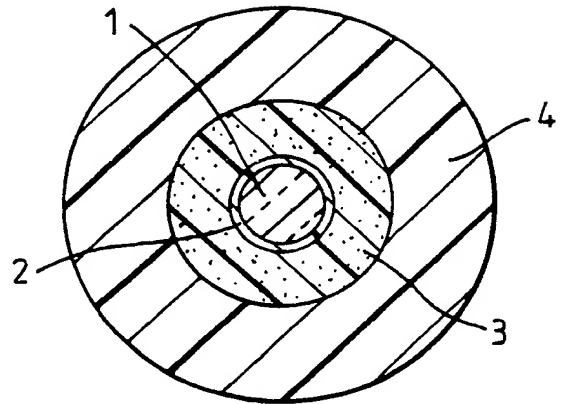


Fig.C.

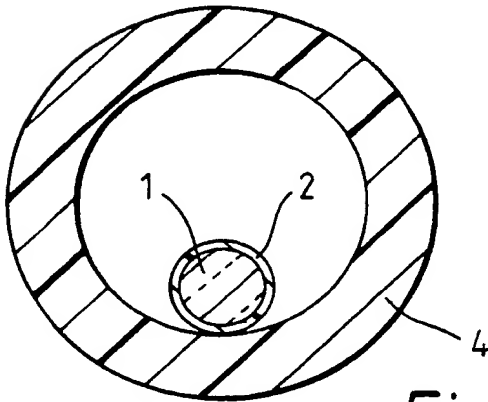
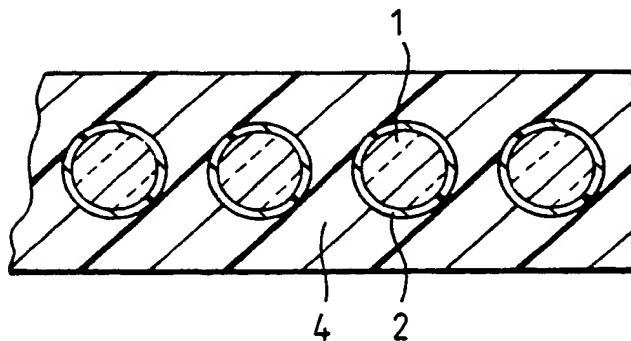


Fig.D.



OPTICAL WAVE-GUIDES

The present invention relates to the use of thermoplastically-processable mixtures of polyamides for the production of polymeric protective layers for optical wave-guides. A protective layer may be produced by
5 extrusion, and joined to an optical wave-guide core and possibly further layers composed of polymers or other materials, to form optical wave-guide cables.

Fibres for optical transmission are generally
10 composed of a special "optical" glass which is a brittle material. To improve its inadequate mechanical strength, it is generally provided with a lacquer-like material and a plastic sheath.

However, such an optical fibre cable has various
15 shortcomings. For example, breakages often occur in the fibre cores, and their transmission properties are impaired by external pressures, impact or bending stresses. Other suitable sheathing materials have therefore been sought.

20 US-A-3980390 describes the production of optical fibres by spinning glass fibre from a melt and applying, before it comes into contact with other solid substances, a resin coating on which a further coating composed of a thermoplastic resin composition is in turn applied by
25 melt extrusion. The primary coating of resin composition is applied to the surface of the fibre directly after it has been spun and serves to maintain the original strength of the glass material, while the secondary protective layer provides protection against mechanical
30 stresses, moisture, ultraviolet radiation, etc. An optical fibre produced by this process (type A) is shown in cross-section in Figure A of the accompanying

drawings; Fig. A shows a glass fibre core 1, a primary coating 2 and a secondary protective layer 4.

D. Gloge et al., "Optical fiber packaging and its influence on fiber straightness and loss", BSTJ 54 (1975) 245-262, and J. Geisler et al. "Optical fibers", Appl. Technical Ser. V/S 120 of Pergamon Press (1986), disclose that the transmission properties of optical fibres are subjected to marked variations as the result of micro-bending. There have therefore been attempts to improve the double-layered structure of the sheath of the type of optical fibre shown in Figure A. A typical example (type B) is shown in cross-section in Figure B of the accompanying drawings; Fig. B shows additionally, between the primary and secondary coatings 2,4, a buffer layer 3 of a material which can absorb external stresses or strains and is composed, for example, of polyisobutene, a gel, a foamed plastics material, an ethylene/vinyl acetate copolymer, a conventional commercial silicone resin or a rubber-like material.

In another known type of optical fibre, the internal diameter of the secondary protective layer is greater than the external diameter of the primary coating, so that there is a space between the two coatings. A fibre of this type (type C; having the same components as that of Fig. A) is shown in cross-section in Figure C of the accompanying drawings.

In a further industrial design of optical fibre, the secondary covering is designed as a flat strip in which the optical fibres are arranged next to one another in parallel rows. This design (type D; having the same components as that of Fig. A) is shown in cross-section in Figure D. The advantage of this design lies in the fact that several such strips can be arranged on top of one another, allowing a flexible method of construction.

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In optical fibres of types A to D, the fibre core is mechanically isolated by the primary coating, and possibly also by the secondary protective layer, from external mechanical forces as well as internal or
5 external stresses caused by the differing coefficients of thermal expansion of the various materials of which the optical fibre is composed. Investigations have shown that, in contrast to fibres of types A and D, a slighter increase in transmission losses under the influence of an
10 external pressure or at lower temperatures is observed for fibres of types B and C. Owing to the space between the primary and secondary coating, a type C fibre additionally has high resistance to micro-bending which occurs as the result of an external force or internal
15 thermal stresses. Shrinkage of the secondary coating material in the longitudinal direction may lead to coiled bending of the optical fibre, without causing transmission losses.

Thermoplastic resins which may be extruded as a melt
20 have been used for producing the secondary protective layer. Polyamides, polyesters, polyolefines and fluorine polymers, in particular, can be used, as these materials can easily be extruded, are very resistant to weathering and have high mechanical strength. It is particularly
25 advantageous to use polyamides which have a relatively low coefficient of thermal expansion and low water absorption capacity, and which are therefore also used for the coating of electric wires.

Various investigations have shown that polyamide-12
30 types can be used successfully for producing the secondary protective layer for optical fibres. Such fibres are substantially free from variations in the transmission losses occurring as the result of micro-bending, i.e. free from variations in the
35 transmission losses as a result of the application of the

secondary protective layer by extrusion and as a result of external stresses which occur during sheathing and installation or cable laying. Optical fibres which have a coating of polyamide-12 and related copolyamides whose
5 moduli of elasticity are between 200 and 2200 N/mm² at room temperature are known from DE-A-2512312, DE-A-2723587, DE-A-2724155, DE-A-3144182, DE-B-2914555 and JP 148210/78.

In addition to their resistance to micro-bending,
10 optical fibres must also have stable transmission properties at temperatures of from -30 to +60°C. They must maintain their properties even if used, for example, as underwater cables where high water pressures can occur.

15 This harmful effect can be reduced if a sheathing material having a high modulus of bending elasticity to ensure a sufficiently high resistance to transverse pressure is selected. However, suitable materials frequently have high viscosities, so that the secondary
20 protective layer cannot be extruded at a satisfactory rate. Materials which have good properties and which can be processed at high speeds are therefore desired for inexpensive and industrially simple production.

An object behind the present invention is to
25 overcome the given disadvantages of optical fibre cables having secondary layers, more particularly, the viscosity-dependent irregular thickness of the applied coatings, inadequate resistance to pressure and to buckling, excessive water absorption capacity, reduced
30 resistance to micro-cracks with small bending radius (the phrase "bending radius" meaning the radius of a loop of the fibre cable at which no further damage occurs, for example by buckling or micro-cracks, which would lead to transmission losses), defective dimensional stability due
35 to after-crystallisation of the polymer,

and inadequate mechanical strength. All these characteristics can increase transmission loss, and/or make production uneconomical.

An optical wave-guide according to the invention
5 comprises a core and a cladding in which the latter comprises a thermoplastically-processible mixture of
I) from 0 to 95% by weight of polyamide-12;
II) from 50 to 5% by weight of a polyamide elastomer;
and
10 III) from 0 to 95% by weight of a further polyamide and/or copolyamide.

The polymeric protective layers to be used according to the invention are preferably produced by extrusion, and are joined in any desired manner to the core and,
15 often, further layers composed of polymers or other materials. The mixture of components I, II and III is preferably used for producing the so-called secondary protective layers of optical waveguides.

The term polyamide-12 (I) covers all materials which
20 have been obtained by known processes by polymerisation of laurolactam or by polycondensation of ω -aminolauric acid. Polyamide-12 can also contain relatively small proportions by weight (usually about 0.1 to 5% by weight) of radicals derived from chain length-regulators, i.e.
25 substances which limit the molecular weight to specific values. Dicarboxylic acids or diamines, for example, act as chain length-regulators.

The relative viscosity of the polyamide-12 which is to be used according to the invention is a measure of its
30 molecular weight; it is preferably between 1.4 and 2.1, more preferably between 1.5 and 1.8, measured in m-cresol under the conditions described in DIN 53727.

The polyamide elastomers (II) which represent a substantial constituent of the mixtures to be used in the
35 invention can originate either from the class of

polyetheramides of the type described, for example, in DE-A-3006961 or in CH-A-0656135 or from the class of polyetheresteramides such as in DE-A-2936977 or DE-A-3428404.

5 Suitable polyetheramides can be produced by known processes from

- a) ω -aminocarboxylic acids or lactams containing more than 10 carbon atoms,
- b) α, ω -diaminopolyalkylene oxides having molecular
10 weights of between 230 and 2500, of which the
 alkylene radicals are linear or branched and contain
 at least 3 carbon atoms, and
- c) C₆₋₃₆ dicarboxylic acids, in an amount equimolar
 with component b).

15 Such polyetheramides can also contain a small quantity of molecular radicals resulting from mono- or tricarboxylic acids or from mono- or triamines. The proportion of polyalkylene oxide units originating from component b) (polyether blocks) in the polyetheramide is
20 from 5 to 60, preferably from 10 to 45% by weight, based on the total weight of the polyetheramide. The relative viscosity of the polyetheramide lies between 1.4 and 2.1, preferably between 1.5 and 1.9, under the conditions given above for polyamide-12.

25 Suitable polyetheresteramides can be produced from

- a) ω -aminocarboxylic acids or lactams containing more than 10 carbon atoms
- b) α, ω -dihydroxypolytetrahydrofurans having molecular
 weights between 160 and 3000, and
- 30 c) dicarboxylic acids in an amount equimolar with
 component b).

 The proportion of polytetrahydrofuran units derived from b) in the polyetheresteramide is from 5 to 50% by weight, preferably from 10 to 45% by weight, based on the
35 total weight of the polyetheresteramide. The relative viscosity of the polyetheresteramide is as given for the polyetheramides described above.

The other polyamides and/or copolyamides (III) used in the invention may be obtained by polycondensation or polymerisation of ω -aminocarboxylic acids (such as ω -aminocaproic acid, ω -aminoundecanoic acid and, in the case of copolyamides, also ω -aminolauric acid) and lactams (such as caprolactam and also, in the case of copolyamides, laurolactam) or by reaction of monomers which react with one another, such as a diamine and a dicarboxylic acid, or from mixtures of the above-mentioned compounds.

Hexamethylenediamine, nonamethylenediamine, decamethylenediamine, dodecamethylenediamine, 2,2,4- and 2,4,4-trimethylhexamethylenediamine, isophorone diamine, bis(aminocyclohexyl)alkanes and alkyl derivatives thereof, as well as xylylenediamines, for example, can be used as diamines. Adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, brassidic acid, dimerised fatty acids, terephthalic acid, isophthalic acid, substituted isophthalic acids and cyclohexanedicarboxylic acid, for example, can be used as dicarboxylic acids.

The relative viscosity of the polyamides and copolyamides (III) obtainable in this way lies between 1.4 and 2.1, preferably between 1.5 and 1.8, measured in m-cresol under the conditions specified above.

Component (III) is neither polyamide-12 nor a polyamide elastomer. Examples of suitable materials are given in GB-A-1548431, GB-A-2170209 and GB-A- (Pat.App. 8629928). It is optional, in the sense that the mixture may comprise components I and II only; that is often preferred. The mixture may alternatively comprise components II and III only.

The mixture of components can be used in the form of a quantity of granulate (dry blend) or in the form of a

polymer alloy for producing polymeric protective layers of optical waveguides by extrusion.

Additives such as antioxidants, UV-stabilisers, dyes, pigments and lubricants can be added in small quantities to the mixtures used in the invention.

There are various advantages associated with the invention:

1) owing to the low viscosity of the mixtures used according to the invention, very high extrusion rates of, for example, 250 m/min and higher can be achieved, and that is possible with comparison products such as polyamide-12 only with a marked deterioration in the general level of quality,

2) as the extrusion rate increases, the light transmission loss (attenuation) only increases slightly and to a far lesser extent than with comparison products such as polyamide-12 (this discovery is of decisive importance for optical wave-guide sheaths),

3) owing to the low dependence of the modulus of bending elasticity on irregularly varying temperatures, very high constancy and independence of temperature in the resistance to transverse pressure and buckling are achieved,

4) owing to the increase in the extrusion rate, the crystallisation tendency of the material diminishes markedly and an improvement is thus achieved in the dimensional stability (whereas stresses which increase attenuation are released in optical wave-guide cables by polymers which crystallise later, such as polyamide-12),

5) substantially less pressure-sensitivity is found in the optical wave-guide sheath than in products such as polyamide-12, while the extrusion rate increases and the attenuation values remain substantially constant,

6) flexibility and resiliency are improved, owing to the polyamide elastomer content (these properties are advantageous for certain optical wave-guide cables),

7) water permeability is 20 to 25% lower than that of polyamide-12 products of similar viscosity, owing to the polyamide elastomer content.

The following Examples illustrate the invention.

5 All parts and ratios are by weight.

Example 1

This Example illustrates the constant dimensions of a tube of small cross-section which has been produced by extrusion at low to very high take-off speeds using,
10 according to the invention, an 83:17 mixture of polyamide-12 (I) and a polyamide elastomer (II). The polyamide-12 (I) was obtained by conventional polymerisation of 99.4 parts laurolactam and 0.6 parts adipic acid, and had a relative viscosity of 1.6.

15 The polyamide elastomer (II) used was produced in a similar manner from 65.6 parts laurolactam, 19.5 parts dimerised fatty acid (Pripol 1014 manufactured by Unichema, Emmerich), 14.35 parts polyoxypropylenediamine having a molecular weight of 420 (Jeffamine D 400
20 manufactured by Texaco) and 0.3 parts polyoxypropylene-triamine having a molecular weight of 450 (Jeffamine T 403 manufactured by Texaco) in the presence of 0.25 parts of a conventional commercial sterically-hindered phenol as antioxidant (Irganox 1098 manufactured by Ciba-Geigy,
25 Basel), and had a relative viscosity of 1.65.

The components I and II were mixed in the melt in the specified ratio, and then processed on a single-screw extruder (manufacturer Schwabenthan, Berlin) with a screw diameter of 45 mm and a L/D ratio of 25 at a melt
30 temperature of 220 to 245°C, to give a tube having an external diameter of 2.5 mm and an internal diameter of 2.2 mm. The take-off speed could be increased from 50 m/min to 270 m/min without any change in the dimensions of the tube at any speed. The dimensions of the tube
35 were therefore independent of the take-off speed.

Comparison Example 1

A tube was produced from 100% of the polyamide-12 used in Example 1 on the same extruder as in Example 1 under comparable extrusion conditions. The dimensions of this tube were also adjusted to an external diameter of 2.5 mm and an internal diameter of 2.2 mm. Perfect tubes could only be obtained up to a take-off speed of 160 m/min. Problems arose at a higher take-off speed; for example, the diameter of the tube varied and it frequently collapsed. The production of a tube of polyamide-12 having a relative viscosity of 1.65 (commercial product of inexactly known composition) produced similarly undesirable results.

Example 2, Comparison Examples 2a and 2b

A glass fibre coated with a primary silicone resin layer of unknown composition was provided with a secondary polymeric protective layer (sheath) using the 83:17 polyamide-12/polyamide elastomer described in Example 1 on the test apparatus described in more detail below. The diameter of the glass fibre was 125 μ m and the thickness of the primary protective layer 140 μ m.

For comparison purposes, the same glass fibre was also sheathed with the same polyamide-12 type as in Comparison Example 1. Comparison Example 2a relates to the use of polyamide-12 from laurolactam and adipic acid having a relative viscosity of 1.6, and Comparison Example 2b to the use of a conventional commercial polyamide-12 of unknown composition having a relative viscosity of 1.65.

The test apparatus was made up of a stress regulator, a single screw extruder manufactured by Maillefer and having a transverse injection head (screw diameter 45 mm and L/D ratio 24), a device for controlling measurement of the cross-section of the secondarily-sheathed glass fibre, a cooling zone with two

water baths at 40 and 15°C respectively, a blower for removing retained water, a take-off device and winding units with bobbin for the glass fibre/optical wave-guide.

The glass fibres were sheathed with the polymer mixture or the comparison materials at various glass fibre input speeds and glass fibre cable take-off speeds.

The following properties were measured in the finished glass fibre cables:

- 1) Optical transmission loss (= attenuation) at -30°C in dB/km for 1300 m wavelength after the optical waveguide cable had been exposed twice to the following temperature cycle: 1 hour at 20°C, 1 hour at -30°C and 1 hour at 60°C.
- 2) External load which causes attenuation of 0.01 dB/km as a function of the extrusion rate.
- 3) Attenuation as a function of the bending radius at 20°C.

The following results were obtained for the light transmission loss at -30°C as a function of the extrusion rate according to the given temperature cycle (the specified values represent minima and maxima of 10 measurements in each case):

	Extrusion rate [m/min]	Attenuation [dB/km]		
		Example 2	Example 2a	Example 2b
25	50	0.02-0.17	0.11-0.98	0.1 -0.4
	100	0-0.08	0.08-0.32	0.08-0.18
	150	0-0.06	0.08-0.28	0.08-0.15
	200	0-0.05	0.08-0.20	0.08-0.1

The results show that the transmission loss decreases in all cases as the extrusion rate increases, but that particularly low values are obtained when using the polymer mixture of polyamide-12 and the polyamide elastomer. The polymer mixture could be processed at higher extrusion rates than those specified (for example,

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250 and 300 m/min), and this was not possible when using the comparison products.

The following results were obtained for the external load which causes attenuation of 0.01 dB/km as a function of the extrusion rate, calculated per glass fibre cable length:

Extrusion rate		External load [kp/mm]		
[m/min]		Example 2	Example 2a	Example 2b
10	50	1.5	1.2	1.2
	100	1.4	1.1	1.0
	150	1.3	1.0	0.9
	200	1.3	0.9	0.9

These results show that the same attenuation value is attained in the optical wave-guides of Example 2 at a higher external load than for the comparison materials. Moreover, the loadability of the optical waveguide cables generally decreases as the extrusion rate increases but to a much lesser extent in the case of cables with the polymer mixture as secondary protective layer.

The following results were obtained for the bending radius which causes attenuation of 0.01 dB/km as a function of the extrusion rate:

Extrusion rate		Bending radius [mm]		
[m/min]		Example 2	Example 2a	Example 2b
25	50	15	30	30
	100	20	25	30
	150	20	25	30
	200	20	25	25

These results show that the optical wave-guides of Example 2 allow the smallest bending radii. This simplifies installation of those optical wave-guides which have been produced using the polyamide-12/polyamide elastomer mixture as secondary protective layer.

CLAIMS

1. An optical wave-guide comprising a core and a cladding, in which the cladding comprises a thermoplastically-processable mixture consisting of
 - I) from 0 to 95% by weight of polyamide-12,
 - II) from 5 to 50% by weight of a polyamide elastomer, and
 - III) from 0 to 95% by weight of another polyamide and/or copolyamide.
2. An optical wave-guide according to claim 1, in which the polyamide elastomer is a polyetheramide which has been produced from
 - a) an ω -aminocarboxylic acid (or a lactam thereof) containing more than 10 carbon atoms,
 - b) an α, ω -diaminopolyalkylene oxide having a molecular weight of between 230 and 2500, the alkylene radicals being linear or branched and containing at least 3 carbon atoms, and
 - c) a dicarboxylic acid containing from 6 to 36 carbon atoms, in an amount equimolar to component b).
3. An optical wave-guide according to claim 1, in which the polyamide elastomer is a polyetheresteramide which has been produced from
 - a) an ω -aminocarboxylic acid (or lactam thereof) containing more than 10 carbon atoms,
 - b) an α, ω -dihydroxypolytetrahydrofuran having a molecular weight of between 160 and 3000, and
 - c) a dicarboxylic acid, in an amount equimolar to component b).
4. An optical wave-guide according to claim 2, in which the polyetheramide is composed substantially of laurolactam, α, ω -diaminopolyoxypropylene oxide and a dimerised fatty acid.

5. An optical wave-guide according to any preceding claim, in which the mixture consists of components I and II.

6. An optical wave-guide according to any preceding
5 claim, in which the mixture consists of components II and III.

7. An optical wave-guide according to claim 1,
substantially as described in any of the Examples.

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